Transport of Gas and Solutes in Permeable Estuarine Sediments

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LONG-TERM GOALS

The long-term goals are 1) to assess the role of small gas bubbles in shallow sandy coastal sediment for sediment geotechnical properties, the transport of solutes across the sediment-water interface and the biogeochemical processes in the sediment surface layer 2) to develop and apply an acoustic technique for the detection and quantification of small gas bubbles in sandy sediment at a high spatial resolution.

OBJECTIVES

1) Quantification of small gas bubbles in the surface layer of coastal sand sediment and assessment of their temporal and spatial distribution.
2) Quantification of the volumes and composition of the gas bubbles in the sediment and the overlying water and the changes of volume and composition over time.
3) Measure the dispersion and transport of solutes caused by bubble volume change and migration under different pressure conditions.
4) Develop and apply an acoustic technique with high spatial and temporal resolution for the detection and quantification of embedded gas bubbles

APPROACH

The project combines instrument development with laboratory and field measurements.

- We developed a **hand-held ultrasound device for the detection of small gas bubbles** embedded in sandy sediment. This device was tested in the laboratory and in the field, and its functionality is demonstrated by measuring the spatial and temporal distribution of small bubbles produced by photosynthesis in sublittoral sands.
- We developed an **instrument for the application of realistic pressure oscillations to incubated sediment cores** with gas enclosures. This instrument is used to quantify the effect of buried bubbles on sediment properties and interfacial solute exchange.
- We measured of **gas release volumes** from sandy sediments using benthic chambers and bubble traps. While the chambers allowed changing the advective transport component and thereby also

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gas ebullition, the bubble traps collected bubbles under the natural flow conditions. The composition of the sampled gas volumes is analyzed using a Gas Chromatograph (GC).

- We conducted **gas-stripping experiments** in laboratory column reactors filled with natural sands and in the field using gas injection techniques that test the gas stripping caused by nitrogen and oxygen ebullition.
- **Content, distribution and migration of free gas in the surface layers of the sand** sediment was investigated with a tunable ultrasound square wave pulser, with measurement rate adjustable from 10 Hz to 1000 Hz in 10 Hz increments connected to one sending and one receiving high-frequency transducer (1 MHz).
- **Measurement of solute transport caused by bubble compression and migration.** This process was investigated in the field using benthic chambers and a laboratory column setup which allowed measurement of the migration behavior and velocities of gas bubbles in permeable sandy sediments under the influence of sinusoidal pressure oscillations and determination of transport rates, dispersion and interfacial flux of solutes and colloidal material.

For a more detailed description of the methods and technologies used in this project and results in the previous years we refer to the first three annual reports. Below a summary of the work completed within the reported project year 2011/2012.

WORK COMPLETED

Compilation of thesis and manuscripts

We are within the last year of our project and we therefore emphasized data analysis and compilation of findings. Our instrument development work, the design and testing of an acoustic system that can detect and quantify small gas bubbles buried in sandy sediments (Fig. 1), was published in spring 2012. Graduate student Chiu Cheng wrote his Master's thesis addressing the results of the field measurements and laboratory experients on bubble ebullition and will defend in October. The chapters of the thesis presently are prepared for publication. Graduate student Lee Russell expands the research of Cheng, and is investigating the influence of pressure oscillations on the sedimentary bubbles, gas exchang and fluid fluxes and will produce his Ph.D. dissertation based on this reserach.

The acoustic method for detecting and measuring small gas bubbles in marine sands.

This method and instrument were developed in this project and are now published (*1*). The publication introduces the high frequency acoustic instrument for the detection and quantification of small free gas volumes in sandy coastal sediments. After introducing and explaining the instrument, the paper presents the results of the field measurements carried out in St. Joseph Bay. A publication of research group related to this work explains the instrument developed for the oxygen flux measurements conducted at St. Joseph Bay(*2*).

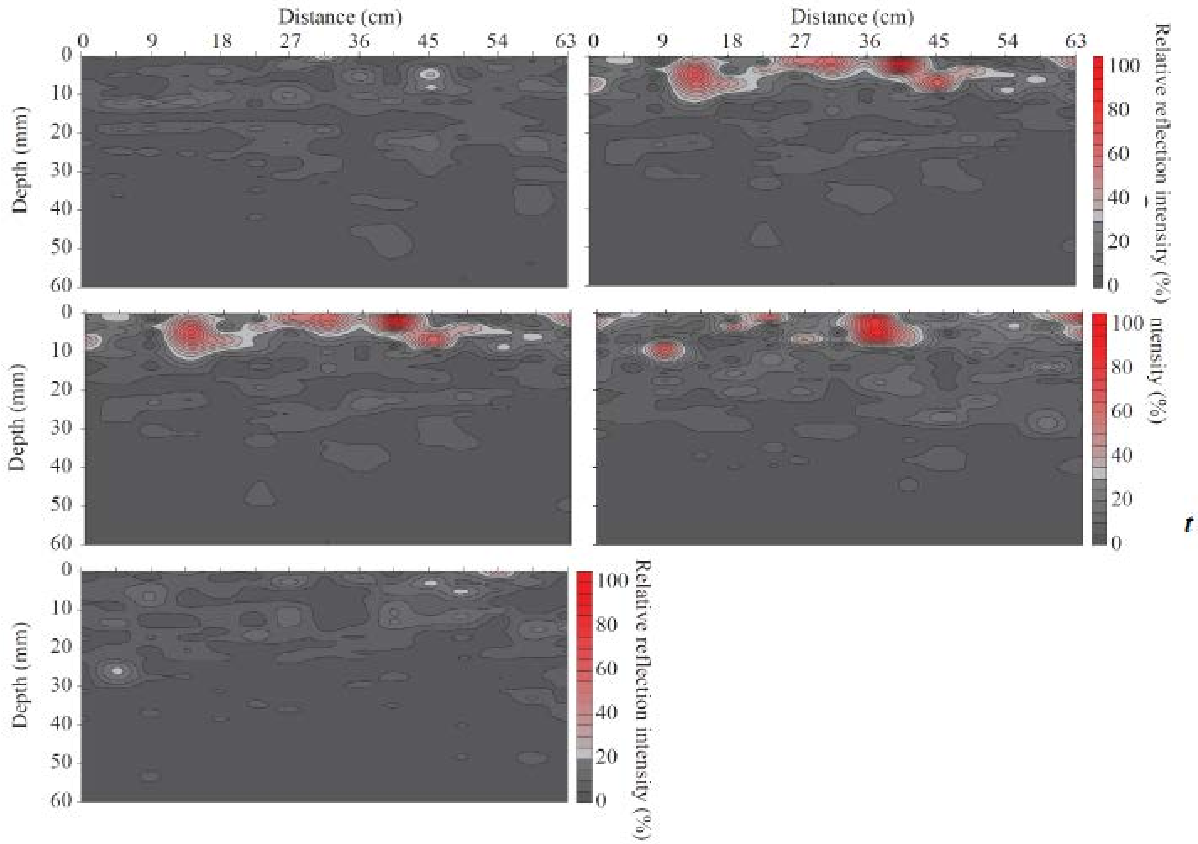


Fig. 1. Acoustic scans conducted at St. Joseph Bay, Florida. The left pane represents sediment shortly after sunrise, the right pane sediment after 3 h sunshine. Red areas are areas of high acoustic reflectivity caused by oxygen bubbles.

Quantification of bubble release volumes and composition

Gas traps were re-deployed to capture photosynthetically-produced bubbles released from coastal sediments and to quantify gas volume and composition. Gas samples were stored in gas-tight vials and measured on a Shimadzu gas chromatorgraph-8A TCD for oxygen and nitrogen percentages. In addition, sediment samples were collected and free gas was extracted through gentle resuspension of the sediment and trapping of emerging bubbles. The main goal of these gas collections was to generate data that can be compared with our gas stripping laboratory experiments.

Gas stripping by sedimentary bubbles and bubbles travelling through the water column

Oxygen bubbles produced by photosynthesis in the sediment affect the concentrations of dissolved gases in the pore water. As soon these oxygen bubbles are generated within the sediment, they exchange gases that are dissolved in the pore water according to the partial pressures in the surrounding fluid. As the bubbles are very small (< 5 mm diameter) the exchange is relatively rapid and thus effective. In order to quantify this process, we collected gas bubbles from sediments and water column and analyzed them for their gas composition. In order to quantify the gas stripping

process for well-defined settings, we conducted gas stripping experiments in the field. These gas stripping experiments addressed the potential of sediment and water column and were conducted at St. Joseph Bay/Florida in May, 2012. Bubbles composed of pure oxygen gas with a total volume of 10 ml per bubble set were released at the sediment water interface and captured after rising either 20, 40, 60, 80 or 100 cm through the air-saturated water column. The bubbles had a 6 mm diameter when released at the sediment surface. In a second set of experiments, bubbles with 5 mm diameter were released. Collected gas was stored in 8.4 ml GC vials. Each bubble-rising distance was collected in triplicates. In a second set of in-situ experiments, 10 ml oxygen gas was injected into the sediment at 2 cm depth, where bubbles resided for approximately 10 seconds before ebullition occurred. The rising gas bubbles were then collected at the same depth intervals in the water column as in the previous experiment. The diameter of bubbles released from the sediment was on average 7.2 mm diameter. The composition of the trapped gas samples was analyzed in the lab on a gas chromatograph.

Diffusive gas stripping by bubbles in sediment or seawater

The purpose of these experiments was to determine the changes in gas composition in bubbles embedded in natural sediment or natural seawater under controlled temperature conditions through diffusion. The gas exchange between bubbles and their surroundings is a function of the transport processes at the bubble-water interface and these transport processes include diffusion and advective processes, i.e. when turbulence reduces the thickness of the diffusive boundary layer at the bubble-fluid interface. These experiments were initiated in order to separate diffusive and advection-enhanced bubble gas exchange. Sediment and seawater originated from the same site as used for the field study. Gas volumes of 5, 10 and 15 ml of pure oxygen gas were exposed to either water saturated sediment or seawater. Sediment and water were kept at a temperature of 25°C. The water was air saturated while the sediment was only oxic in the upper 10 mm and anoxic below that layer. Each treatment within the experiment contained triplicates for each sampling point. Gas was sampled after 1, 3, 10 and 24 hours and analyzed on the GC TCD with the molecular sieve 5A and Carboxen-1000 columns.

Assessment of bubble response to pressure oscillations in transparent sediment

The gas bubbles embedded in the sediment surface layer respond to pressure changes as caused by surface gravity waves, tides or atmospheric pressure changes. In order to assess the effect of pressure-induced bubble volume changes on the fluid movement in permeable sediment, gas bubbles in the millimeter-size range were introduced into Nafion sand, a substance with similar refractive index as water. Nafion grains thus can be used to produce sediments with high transparency. Bubbles of known gas volume were embedded in water-saturated Nafion sediment and exposed to a steady hydrostatic pressure as experienced in the shallow sublittoral zone and pressure oscillations as caused by surface gravity waves. The latter were produced in the instrument we developed to simulated wave pressure oscillations by a computer-controlled linear motor controlled. The effect of the pressure on the bubble was quantified using high-frequency digital imaging. The individual pictures were analyzed using an image analysis software producing calibrated bubble volumes for known pressures.

RESULTS

Gas stripping caused by photosynthetic oxygen bubbles produced in coastal sediment

Oxygen concentration in water column bubble samples ranged from 14% to 66%, with the measurable remainder consisting of N_2 gas only. In the sediment this range was 8% to 64%, with the remainder as

N_2. In sediment and water column bubbles, the rate of increase in oxygen concentration was the greatest between 6:00 and 12:00. Oxygen concentration maxima were reached in the early evening (18:00). The rates of decrease in bubble oxygen concentration after sunset were greater in the sedimentary gas bubbles. Bubble formation trailed light because the oxygen has to build up to supersaturation within the sediment before bubbles are formed that then are later released through ebullition. The daytime average oxygen concentrations in sedimentary bubbles were typically higher than those of water column bubbles. The opposite was recorded during the dark phases.

Measureable amounts of oxygen were lost from gas bubbles released at the sediment-water interface after travelling 40 cm through the water column. When bubbles were released at 2 cm sediment depth, 2 percent of the oxygen was already lost at 20 cm above the sediment revealing the stronger stripping effect in the sediment due to the lower pore water oxygen concentrations. After travelling 1m through the water column, the oxygen concentration in 7 mm diameter gas bubbles dropped by up to 20%.. Typically, the larger the volumes of gas produced, the higher the percentage of oxygen present in the bubbles (Fig. 2).

During summer, when gas production was highest, volume and oxygen concentration in bubbles peaked (Fig. 2). A stronger correlation between sediment gas data and temperature underlined the temperature effect on bubble formation. In November, we observed the lowest oxygen concentrations (~8%) in the sediment samples in the evening (24:00 and 6:00) compared to any of the water column samples in our seasonal time series, indicating the highest gas stripping rates in the sediment. At night, the oxygen levels in our sediment samples were always lower than the oxygen values measured in the water column. When the oxygen concentrations in the gas bubbles are averaged over the course of the summer, they were slightly higher in the sediments (35-45%) than in the water column (28-34%)

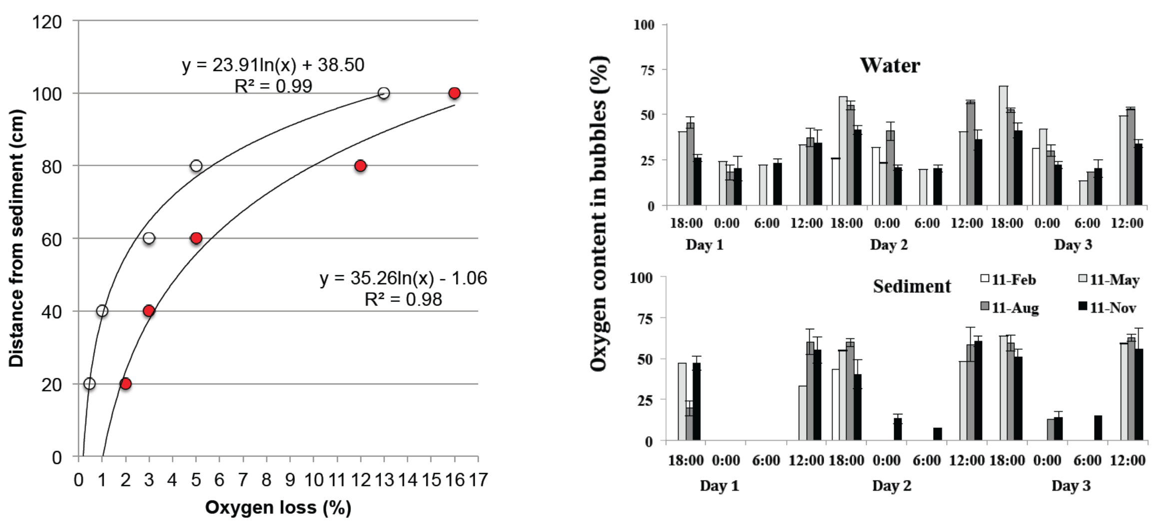


Fig. 2. Left: Oxygen stripping from rising gas bubbles measured at St. Joseph Bay, Florida. White circles show stripping from oxygen bubbles released at the sediment surface. Red circles show stripping from oxygen bubbles released 2 cm below the sediment water interface. These bubbles lost already 1% of their oxygen when they reached the sediment surface. Right: Oxygen content (%) in bubbles sampled from water column (upper graph) and sediment (lower graph). Error bars depict standard deviation.

Diffusive gas stripping by bubbles in sediment or seawater

The laboratory tests confirmed the in-situ results showing a stronger gas stripping in the sediment compared to oxygen losses of water column bubbles, i.e. gas exposed to sediment was stripped 33 to 40 percent more of the oxygen compared to the same volume of gas in the water column (Fig. 3). The results from the diffusive stripping experiments are used to estimate the gas stripping caused by advective components, i.e. the movement of the ascending bubbles through the water. For these calculation, the gas exchange has to be normalized to exchange surface area and pressure, and presently we are in the process doing these calculations.

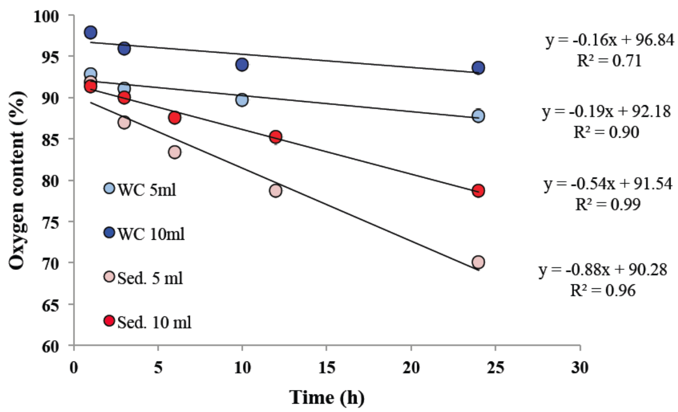
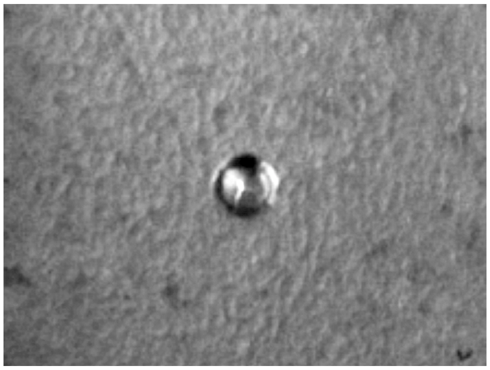


Fig. 3. Left: Oxygen stripping from gas bubbles in stagnant water (blue circles) and sediment (red circles) from the study site. Dark colors indicate 10 ml gas volume, light colors 5 ml gas volume. The water was air saturated during the experiment.

Assessment of small bubble response to pressure oscillations

The hydrostatic pressure imposed by a 1 m water column reduced the size of bubbles with defined volumes ranging from 1 to 10 microliter at atmospheric pressure and embedded at 1 cm sediment depth by 20%. When these small sedimentary bubbles were subjected additional pressure oscillations equivalent to those caused by surface gravity waves of 1 m amplitude, the volume of the bubbles was reduced by another 17% (Fig.4). The hysteresis with faster compression of the bubbles and slower expansion, caused by the limited elasticity of the sediment, resulted in variability of the compression/expansion values of ±3.0 to ±3.5%. This limited elasticity of the permeable sediment, in which the bubbles are embedded, is crucial for the pumping effect of oscillating bubbles as the relatively rapid volume change of the bubble cannot be compensated by sediment movement. Volume compensation thus has to proceed through pore water movement and the water flows along the path of least resistance, which is typically directly to the sediment-water interface.



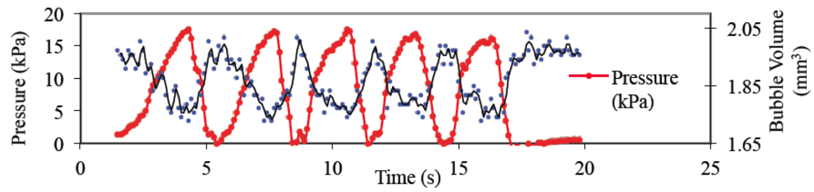


Fig. 4. Left: Air bubble (2 ul) embedded in transparent Nafion sediment. The bubble is located in the center of a container approxiamtely 1 cm away from the wall of the container. Right: Response of the embedded bubble to pressure fluctuations. The bubble was initially exposed to a hydrostatic pressure of 1 m water column and then to an additional 1 m water column pressure oscillation.

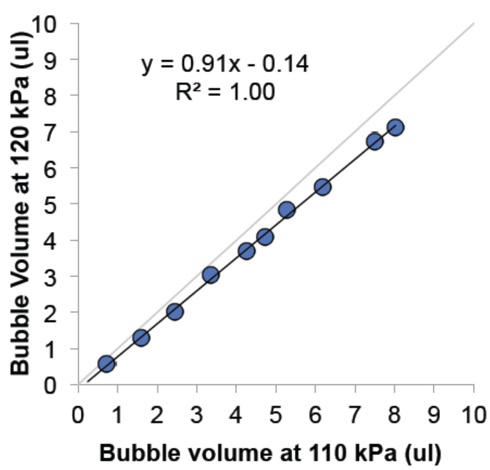


Fig. 5. Response of an air bubble embedded in Nafion sediment to an increase in pressure by 10 kPa during passage of surface gravity waves. The bubble volume decreased by approximately 10%.

IMPACT/APPLICATIONS

The results from the gas stripping measurements reveal the effectiveness of the sedimentary bubble formation and ebullition for the transfer of gases from shallow sediment to the overlying water and atmosphere. Because the bubbles ascend rapidly through the water column, gas exchange between water column and the small bubbles is effective, providing a pathway for sedimentary gases to the cycling of matter in the water column. Our work shows that the sedimentary bubble genearation proceeds through distinct dayly cycles, with a buildup of bubbles mostly during the afternoon and consumption of bubbles after sunset. Despite this consumption, bubbles are present in the sediment until midnight and thus can act as reservoirs for oxygen for the benthic community. This buffering

effect is facilitated by the high abundance of the bubbles that reached up to 100,000 per m^2 in our study area. As the majority of these bubbles is very small (<5 mm diameter) the gas stripping process is effective and changes the gas composition in the bubbles significantly before ebullition occurs. The small volume of the bubbles reduces rise velocity while enhancing exchange of gas in the water column. The bubbles released from the sediment thus are effective in coupling sedimentary and water column gas dynamics. The pressure oscillations caused by waves, tides and atmosphere affect the bubbles buried in the sediment and our studies show that they respond instantly to these pressure changes with volume changes. Despite their small size, the large abundance of these bubbles in the sediment their volume change makes them effective for pore water mixing and interfacial solute fluxes. We presently are quantifying these effects in our computer-controlled pressure chamber. We expect that the results will show an effective increase in sediment water exchange of solutes caused by the bubbles.

The development, movement and volume changes of the bubbles in shallow coastal sediments have implications for sediment geotechnical properties. The compactability of the sediment is increased and the bubbles formation presents a mechanism of dayly compressibility changes of the surface sediment layer. These compressibility changes not only affect support strength of the sediment but also acoustic properties related to the changes in permeability caused by the bubbles and the reflection of the bubbles. Future research will address the influences of the bubbles as oxygen reservoirs in the sediment and their impact on biogeochemical processes that affect sediment structure and sediment-water exchange processes.

TRANSITIONS

The results of our studies show that the small bubbles generated by photosynthesis in the surface layer of shallow sediments have broad implications for sediment geotechnical, geochemical and biological properties. Through changing sediment structure and pore water circulation, the bubbles influence the sediment erosion threshold, biogeochemical zonations, living space for organisms and thereby the role of the sediments in the cycles of matter. The results are relevant to sedimentologists, benthic ecologist and oceanographers who seek a better understanding of the ecological functioning of the shallow nearshor environment and the possible implications of sea level rise and global warming. Our results on gas stripping and gas exchange introduce new insights in a process that so far has not been included in our modeling of coastal cycles of elements. These results thus can open a new field of research addressing the role of bubble ebullition for benthic-pelagic coupling and element cycling. Our highly sensitive bubble detection method may be applicable in medical sciences and industrial production processes where bubbles can cause problems. When operated by an underwater vehicle, this detection method may also be useful in detecting reflecting objects buried in the sand.

RELATED PROJECTS

NSF project "Collaborative Research: Eddy Correlation and chamber measurements of benthic oxygen fluxes in permeable sediments," $343,385 (Huettel funds), P. Berg, (PI), M. Huettel (co-PI). This project was awarded as a follow-up of our second eddy correlation project (OCE-536431) and supported continuation of our research and instrument development related to the eddy correlation technique for the measurement of oxygen flux in permeable coastal sediment. Within this project, we deployed the eddy flux instrument at our ONR project field sites in order to produce data on oxygen flux that can be compared with the fluxes produced by bubble ebullition. Data from these sites have

provided both new insights on benthic oxygen metabolism and a demonstration of the advantages of the eddy correlation technique in diverse environments.

Within the GRI-funded project: "The Deep-C Consortium: Deep Sea to Coast Connectivity in the Eastern Gulf of Mexico" $203,471 (Huettel funds), E. Chassignet (PI), M. Huettel (one of several Co-PIs), we investigate the effect of the input of old (i.e. crude oil) and new (i.e. phytoplankton detritus) organic matter on sediment properties and biogeochemical reactions. As crude oil from the recent oil spill in the Gulf and phytoplankton affect the sediment in the shallow nearshore zone, this project is closely linked to our research within the ONR project. Specifically, hydrocarbons alter sediment cohesiveness and permeability, thereby altering the effect of the oxygen bubbles on sediment water exchange. Bubble ebullition is restricted while crude oil pollution can limit benthic primary production through toxic components but at lower concentration also enhance the production by increasing microbial growth and associated mobilization of nutrients.

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PUBLICATIONS

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